NASA TECHNICAL NOTE

NASA TN D-6812

NASA TN D-6812

PROBLEM OF PHOTOCHEMICAL EQUILIBRIUM OF OZONE IN PLANETARY ATMOSPHERES: OZONE DISTRIBUTION IN THE LOWER ATMOSPHERE OF MARS

by Shardanand and Gerald Grams

Wallops Station
Wallops Island, Va. 23337

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1972

1. Report No. NASA TN D-6812	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle: Problem of Photochemical Equilibrium of Ozone in Planetary Atmospheres: Ozone Distribution in the Lower Atmosphere of Mars		5. Report Date: May 1972
		6. Performing Organization Code
7. Author(s): Shardanand and Gerald Grams*		8. Performing Organization Report No. WI-100
9. Performing Organization Name and Address: National Aeronautics and Space Administration, Wallops Station, Wallops Island, Virginia 23337; *National Center for Atmospheric Research, Boulder, Colorado 80302		10. Work Unit No.
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address: National Aeronautics and Space Administration, Washington, D.C. 20546		13. Type of Report and Period Covered: Technical Note
		14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

Several investigators have applied techniques used for the study of the ozone distribution in the terrestrial atmosphere to the atmospheres of other planets. This paper shows that such techniques cannot be applied indiscriminately to calculate photochemical equilibrium distribution of ozone in planetary atmospheres. Limitations associated with some of the earlier treatments of photochemical equilibrium distributions of ozone in planetary atmospheres are discussed, and a technique having more universal application is presented. In addition, ozone concentration profiles for the Martian atmosphere based on the results of the Mariner 4 radio occultation experiment and the more recent results from Mariner 6 and Mariner 7 have been calculated using this approach.

17. Key Words (Suggested by Author(s)): Planetary Atmospheres; Ozone; and Photochemical Processes		18. Distribution Statement: Unlimited	
19. Security Classif. (of this report): Unclassified	20. Security Classif. (of this page): Unclassified	21. No. of Pages: 19	22. Price*: $3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

Problem of Photochemical Equilibrium of Ozone in Planetary Atmospheres: Ozone Distribution in the Lower Atmosphere of Mars

By
Shardanand and Gerald Grams*
National Aeronautics and Space Administration
Wallops Island, Virginia

SUMMARY

Several investigators have applied techniques used for the study of the ozone distribution in the terrestrial atmosphere to the atmospheres of other planets. This paper shows that such techniques cannot be applied indiscriminately to calculate photochemical equilibrium distribution of ozone in planetary atmospheres. Limitations associated with some of the earlier treatments of photochemical equilibrium distributions of ozone in planetary atmospheres are discussed, and a technique having more universal application is presented. In addition, ozone concentration profiles for the Martian atmosphere based on the results of the Mariner 4 radio occultation experiment and the more recent results from Mariner 6 and Mariner 7 have been calculated using this approach.

INTRODUCTION

The basis for quantitative discussion of the photochemical production of atmospheric ozone is the assumption of photochemical equilibrium whereby the number of ozone molecules formed equals the number destroyed in unit time and unit volume. In most studies of equilibrium distributions of ozone, the analysis treats only the photochemical reactions which would occur in an atmosphere of atomic and molecular oxygen (O and O_2) and ozone (O_3) in the presence of inert molecules (M). For this

*Associated with the National Center for Atmospheric Research, Boulder, Colorado.

case, the basic photochemical reactions are:

$$O_2 + h\nu \rightarrow O + O \qquad \alpha_2 \qquad \lambda \leq 2424\ \text{Å} \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M \qquad k_2 \tag{2}$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad k_3 \tag{3}$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad \alpha_3 \qquad \lambda \leq 11{,}800\ \text{Å} \tag{4}$$

$$O + O + M \rightarrow O_2 + M \qquad k_5 \tag{5}$$

where α's represent the probability of dissociation of molecules and k's represent the reaction rate constant. The third body, M, conserves energy and momentum in the reaction. It is not necessary to include reactions involving excited molecules whose contributions to the equilibrium concentrations are negligibly small (ref. 1). The method of Wulf and Deming (refs. 2 & 3; see also Craig, ref. 4) for calculating equilibrium amounts of ozone is commonly used for analyses of the ozone distribution in the terrestrial atmosphere. This method utilizes reactions (1) through (4) only, the inclusion of reaction (5) is regarded to have a negligible effect on the numerical calculations for the altitudes of interest in the terrestrial atmosphere.

The model of ozone photochemistry developed by Wulf and Deming has been applied in several studies of the atmospheres of Mars and Venus. For example, some conclusions about the stratospheric circulation and wind patterns of Mars were derived by Paetzold (ref. 5) from his calculated vertical distribution of ozone. However, Marmo et al. (ref. 6) took exception to the use of this method for the study of the atmosphere of another planet and included reaction (5) in their calculations of the ozone distribution in the Martian atmosphere. Their results demonstrated the importance of the direct association of oxygen atoms by three-body collisions for the Martian atmosphere. In addition to a sharp reduction in the total amount of ozone in the atmosphere, significant differences in the shape of the ozone concentration profile were obtained. The ozone concentration profile calculated by Marmo and his co-workers increased monotonically with decreasing altitude to a maximum at the surface of the planet, as opposed to the ozone-concentration maximum at about 40 km predicted by Paetzold's analysis. Because of the importance of ozone in planetary atmospheres, the system of photochemical reactions leading to the equilibrium concentrations of ozone has been re-examined to better comprehend the implications of this discrepancy.

Photochemical Scheme for Calculations of the Vertical Distribution of Atmospheric Ozone

First consideration is given to the scheme of Wulf and Deming involving reactions (1) through (4) which will henceforth be referred to as the 4-reaction system. Let n_1, n_2, n_3, and n_m be the number densities of O, O_2, O_3, and M, respectively. Then, under conditions of photochemical equilibrium, the rate of change of the concentrations of the various compounds of oxygen will be given by:

$$\frac{dn_1}{dt} = 2\alpha_2 n_2 + \alpha_3 n_3 - k_2 n_1 n_2 n_m - k_3 n_1 n_3 = 0 \tag{6}$$

$$\frac{dn_2}{dt} = -\alpha_2 n_2 + \alpha_3 n_3 - k_2 n_1 n_2 n_m + 2k_3 n_1 n_3 = 0 \tag{7}$$

$$\frac{dn_3}{dt} = -\alpha_3 n_3 + k_2 n_1 n_2 n_m - k_3 n_1 n_3 = 0 \quad . \tag{8}$$

These three equations are not independent since continuity of mass considerations require that

$$\frac{dn_1}{dt} + 2\frac{dn_2}{dt} + 3\frac{dn_3}{dt} = 0 \quad . \tag{9}$$

By a linear combination of equations (6), (7), and (8), the following two independent equations are obtained:

$$\alpha_2 n_2 = k_3 n_1 n_3 \tag{10}$$

$$\alpha_2 n_2 + \alpha_3 n_3 = k_2 n_1 n_2 n_m \quad . \tag{11}$$

When n_1 is eliminated from equations (10) and (11), we obtain the quadratic equation,

$$\left(\alpha_3 k_3\right) n_3^2 + \left(\alpha_2 k_3 n_2\right) n_3 - \alpha_2 k_2 n_m n_2^2 = 0 \quad . \tag{12}$$

In most previous studies, n_3 has been calculated from equation (12) as a function of altitude to give a vertical profile of ozone concentration, using an assumed vertical distribution for the equilibrium values of n_2. In the terrestrial atmosphere, this procedure has been well established for calculating the photochemical equilibrium distribution of ozone in the stratosphere, where most of the atmospheric ozone is known to exist. However, limited knowledge of the composition of the atmospheres of other planets prevents the application of such a simplified scheme as the 4-reaction system to studies of the ozone distribution in those planetary atmospheres. The earth's atmosphere, with oxygen as a major constituent, is decidedly different from the atmospheres of Mars and Venus, for example, which are now regarded to be composed mostly of carbon dioxide, containing only traces of oxygen. Thus, a technique which has been successful in studies of the observed temporal and spatial variations of the ozone distribution in our atmosphere should not be expected to apply with equal success to the atmospheres of other planets. One aspect of the 4-reaction system that is particularly disturbing for studies of the ozone distribution is when equations (10) and (11) are solved to eliminate either n_2 or n_3. Then, the resulting quadratic equation in n_1,

$$\left(k_2 k_3 n_m\right) n_1^2 - \left(\alpha_2 k_3\right) n_1 - \alpha_2 \alpha_3 = 0 \tag{13}$$

is independent of local concentrations of the other oxygen compounds. This implies that n_1, n_2, and n_3 are no longer in equilibrium, contradicting the assumption of equilibrium conditions that led to the derivation of equation (13). This contradiction would indicate that the 4-reaction system does not represent a physically stable condition. Then, the question arises: why has the 4-reaction system been successful in calculating photochemical equilibrium distributions in the Earth's stratosphere? This equation predicts that the number of oxygen atoms is determined only by the reaction rate constants, the local number density of all atmospheric molecules, and the probabilities of dissociation of oxygen and ozone molecules. In special cases, as the Earth's stratosphere, α_2 and α_3 can provide an indirect coupling with the columnar number densities of O_2 and O_3 above the given altitude which, in turn, would be approximately proportional to the local values of n_2 and n_3. The values of α_2 and α_3 are evaluated by integrating over wavelengths λ expressions of the form

$$\alpha_2(z) = \int_0^{2424\ \text{Å}} \sigma_2(\lambda)\,\Phi(z,\lambda)\,d\lambda \tag{14}$$

and

$$\alpha_3(z) = \int_0^{11,800\ \text{Å}} \sigma_3(\lambda)\,\Phi(z,\lambda)\,d\lambda \quad , \tag{15}$$

where σ_2 and σ_3 are, respectively, the absorption cross-sections of O_2 and O_3, and Φ is the solar flux at the altitude z. For the case in which the only absorbing constituents of the atmosphere are O_2 and O_3, the solar flux at normal incidence can be evaluated from the expression

$$\Phi(z,\lambda) = \Phi_\infty(\lambda)\ \exp\left(-\sigma_2(\lambda)\int_z^\infty n_2(z)\,dz - \sigma_3(\lambda)\int_z^\infty n_3(z)\,dz\right) \quad , \tag{16}$$

where Φ_∞ is the solar flux at the "top" of the atmosphere. If the columnar number densities of O_2 and O_3 are large enough to affect the numerical value of the exponential factor in equation (16), as is true in the Earth's stratosphere, an indirect coupling, as described above, is possible. However, for columnar densities of O_2 and O_3 that are smaller than in the Earth's stratosphere, the coupling no longer exists and the contradiction is present. For example, the equilibrium number density of oxygen atoms calculated from equation (13) at 100 km in the terrestrial atmosphere would be approximately 2 orders of magnitude higher than n_m, the actual number density of all atmospheric molecules. The contradiction will also be present for planetary atmospheres in which O_2 and O_3 are no longer the major absorbers of the solar radiation. In that case, equation (16) would be rewritten with extra terms in the exponential factor which may be much larger than the terms that are related to absorption by O_2 and O_3 so that the coupling might again be destroyed. Since the atmospheres of Mars and Venus, for example, have oxygen present only as a trace constituent, it would be expected that the 4-reaction system is unsuitable for calculating equilibrium ozone concentrations in the atmosphere of these planets.

In order to assess the problem in more detail, another aspect of the 4-reaction system is considered. In this part of the analysis, an equation for conservation of mass is introduced,

$$n_1 + 2n_2 + 3n_3 = 2\tilde{n}_2 \qquad , \tag{17}$$

where $\tilde{n}_2$ is a constant which may be regarded as an original number density of oxygen molecules which, under photochemical action, has formed oxygen atoms, oxygen molecules, and ozone molecules. By combining equations (10), (11), and (17), an equation for the local ozone concentration is obtained:

$$n_3 = \frac{\alpha_2(2\tilde{n}_2 - n_1)}{3\alpha_2 + 2k_3n_1} \quad . \tag{18}$$

Solution of this equation for the ozone number density requires a knowledge of the number density of oxygen atoms. By eliminating n_2 and n_3 from equations (10), (11), and (17), the following is obtained:

$$\left(k_2k_3n_m\right)n_1^3 - \left(\alpha_2k_2 + 2k_2k_3\tilde{n}_2n_m\right)n_1^2 - \left(\alpha_2\alpha_3 - 2\alpha_2k_3\tilde{n}_2\right)n_1 + 2\alpha_2\alpha_3\tilde{n}_2 = 0, \tag{19}$$

which, at first glance, would appear to be coupled to the number of oxygen atoms available for establishing a condition of photochemical equilibrium. However, this equation can be factored in the form

$$\left[(k_2k_3n_m)n_1^2 - (\alpha_2k_3)n_1 - \alpha_2\alpha_3\right] \quad \left[2\tilde{n}_2 - n_1\right] = 0 \quad . \tag{20}$$

This result again contradicts the assumption of photochemical equilibrium. A solution based on the first factor is identical with the solution for equation (13) which has already been determined to be contrary to the physical meaning of equilibrium concentrations of oxygen compounds. The solution based on the second factor, $n_1 = 2\tilde{n}_2$, represents complete dissociation of the available oxygen compounds which, again, contradicts the assumption of photochemical equilibrium. Thus, a conservation of mass relation cannot be incorporated meaningfully into the solution of the 4-reaction system. In view of the foregoing discussion, it has been concluded that the 4-reaction system should not be applied without reservation for calculations of the ozone distribution of other planets and that investigations based on such calculations (see, for example, Paetzold (ref. 5) who studied the Martian atmosphere and Fabian and Libby (ref. 7) who studied the Cytherean atmosphere) should be reanalyzed within these limitations.

The system consisting of reactions (1) through (5) and, henceforth, referred to as the 5-reaction system is now considered. As before, the solution of the equations for the rate of change of n_1, n_2, and n_3 for equilibrium conditions leads to two independent equations,

$$\alpha_2 n_2 = k_3 n_1 n_3 + k_5 n_1^2 n_m \tag{21}$$

and

$$\alpha_2 n_2 + \alpha_3 n_3 = k_2 n_1 n_2 n_m + k_5 n_1^2 n_m \quad . \tag{22}$$

Equations (21) and (22), along with the conservation of mass relation represented by equation (17), are then available for solving for equilibrium number densities of the oxygen compounds. These equations may be combined to give the following expression for the number density of ozone:

$$n_3 = \frac{k_2 k_5 n_1^3 n_m^2}{\alpha_2 \alpha_3 + \alpha_2 k_3 n_1 - k_2 k_3 n_1^2 n_m} \quad . \tag{23}$$

If n_2 and n_3 are eliminated from the equations describing the 5-reaction system, a cubic equation in n_1 results:

$$\begin{aligned}\left(k_2 k_3 n_m - 3k_2 k_5 n_m^2 - 2k_3 k_5 n_m\right) n_1^3 - \left(\alpha_2 k_3 + 2k_2 k_3 n_m \tilde{n}_2 + 2\alpha_3 k_5 n_m\right) n_1^2 \\ - \left(\alpha_2 \alpha_3 - 2\alpha_2 k_3 \tilde{n}_2\right) n_1 + 2\alpha_2 \alpha_3 \tilde{n}_2 = 0 \quad .\end{aligned} \tag{24}$$

The solution of equation (24) is coupled to the available oxygen as well as the other photochemical parameters and, therefore, provides the coupling mechanism for the desired condition of equilibrium. Thus, the 5-reaction system is to be preferred since, unlike the 4-reaction system, it does not contain an implicit contradiction of the assumed state of equilibrium. Furthermore, inclusion of reaction (5) has the advantage of increasing the generality of the technique for use in exploratory investigations of photochemical equilibrium distributions of ozone in the atmosphere of other planets. Of course, the 5-reaction system is still not as general as a comprehensive analysis of all possible reactions such as the study of the photochemistry of a CO_2 atmosphere conducted by McElroy and Hunten (ref. 8). However it is pointed out that, for the lower atmosphere of Mars from the surface to about 60 km, McElroy and Hunten assumed, as has been assumed here, that the relative concentration of O_2 is constant with a mixing ratio of 10^{-3}. While the 5-reaction system does not provide the amount of insight as a comprehensive study of the mechanisms which maintain this mixing ratio, it does not have intrinsic value for calculations of the ozone distribution in the lower atmosphere of Mars; and, therefore, such calculations have been performed based on the results of the Mariner 4 occultation experiment as well as the more recent results from Mariners 6 and 7.

Calculations of the Ozone Distribution in the Atmosphere of Mars

Calculations of the vertical distribution of ozone in the atmosphere of Mars based on the 4-reaction system and on the 5-reaction system have been reported by Paetzold (ref. 5) and Marmo et al. (ref. 6), respectively. On the basis of the previous discussion, the results of Marmo and his collaborators are more reliable. However, their atmospheric model has a surface pressure of 25 mb and partial pressures of 470 m STP for nitrogen, 55 m STP for carbon dioxide, and 70 cm STP for oxygen in accordance with the results of Kaplan et al. (ref. 9) and a temperature profile with a surface temperature of $250^{\circ}K$, a lapse rate of $2.9^{\circ}K$ per km, and isothermal conditions above 30 km in accordance with the results of Schilling (ref. 10). This atmospheric model is now outdated; furthermore, solar radiation was limited to the spectral region 1750 to 3000 Å in their calculations. For these reasons, it is now possible to provide better data of the ozone distribution of the atmosphere of Mars. Using an atmospheric model based on the results of Mariner 4 radio occultation experiment (ref. 11) and a computer program incorporating an iteration procedure to obtain self-consistent, steady-state distributions of ozone based on the 5-reaction system, calculations of the ozone content of the Martian atmosphere have been performed. In these calculations, no distinction has been made between $O(^1D)$ and $O(^3P)$ atoms as $O(^1D)$ are not present below about 50 km (ref. 8), the altitude interest of our major concern. The numerical data summarized in Table I were used for the calculations. The composition of the atmosphere was taken to be 99.9 percent carbon dioxide and 0.1 percent oxygen. Vertical profiles of O, O_2, and O_3 are shown in figure 1. Solid lines indicate calculated profiles based on the 5-reaction system and the dashed lines indicate profiles based on the 4-reaction system. The profiles for O graphically portray the problem regarding the 4-reaction system. For the 5-reaction system, O profiles increase with altitude to the point at about 65 km at which almost complete dissociation of O_2 has occurred ($n_1 \approx 2\tilde{n}_2$). However, the O profile for the 4-reaction system increases at a much faster rate and exceeds the value of n_m, which is taken to be the number density of all atmospheric molecules at altitudes somewhat above ~60 km. For the 5-reaction system, the O_3 number density decreases monotonically with altitude and has an entirely different profile than the 4-reaction system. Thus, the maximum concentration of Martian ozone is expected at the surface of the planet. Although the significant differences in atmospheric models results in a surface number density of ozone that is over an order of magnitude smaller than that calculated by Marmo et al. (ref. 6), it is concurred that an ozone maximum exists at the surface of the planet. This is in disagreement with the results of Paetzold (ref. 5) which indicated an ozone maximum at an altitude of about 40 km, based on the 4-reaction system and an atmospheric model similar to that used by Marmo and his co-workers.

Additional calculations were performed to determine the effect of varying the parameters used in the model. None of the parameter variations yielded maximum concentrations of ozone at some altitude above the surface of the planet. The effect of lowering the content of carbon dioxide to 80 percent with 19.9 percent argon or nitrogen and 0.1 percent oxygen was to increase the ozone concentrations at all altitudes by about 20 percent without appreciably altering the shape of the profile. When the oxygen content was increased to 1 percent with 99 percent carbon dioxide, the ozone concentrations were increased by a factor of about 2; a similar increase was found for an atmosphere of 80 percent carbon dioxide, 19 percent argon or nitrogen, and 1 percent oxygen. In addition, the effect of limiting the spectral flux to the 1750-3000 Å wavelength interval to match the calculations of Marmo et al. (ref. 6) was investigated. The resulting numerical values for the ozone number densities were about twice those obtained by using the solar flux from 1350-7100 Å. This discrepancy can be attributed mainly to the dissociation of ozone by radiation in the visible part of the solar spectrum.

Finally, atmospheric parameters obtained from Mariner 6 and 7 radio occultation data have been utilized for calculations of the ozone distribution in the Martian atmosphere. The results of these calculations are displayed in figure 2 as vertical profiles of O, O_2, and O_3 from the surface of Mars to an altitude of 35 km. The atmospheric parameters used in the calculations are those presented by Rasool et al. (ref. 12) for the Mariner 6 and Mariner 7 entry data which correspond to daytime conditions at low and high latitudes, respectively. Results obtained from Mariner 4 data are also displayed for comparison; it is noted that the Mariner 6 and 7 results are not substantially different, with the exception of the calculated ozone concentrations near the surface. Integrated total ozone amounts are calculated to be 1.4×10^{-3}, 7.7×10^{-4}, and 8.8×10^{-4} cm STP for atmospheres corresponding, respectively, to Mariner 4, 6, and 7 results. It is pointed out, partially to give substance to the neglect of photochemical reactions involving CO_2 and CO for calculations of equilibrium concentrations of ozone, that the calculated total ozone amounts are in excellent agreement with observations of the total ozone in the Martian atmosphere. The Mariner 6 and 7 ultraviolet spectrometer experiment detected ozone in the Martian atmosphere (ref. 13). Data from these measurements indicated a total ozone amount that was also about 3 orders of magnitude less than found on earth. These calculations, therefore, corroborate the measurements of ozone in the Martian atmosphere.

TABLE I. - PARAMETERS USED AND THEIR SOURCES

PARAMETERS	SOURCES
Mariner 4	
Surface temperature	
(a) All CO_2 -- $180^{\circ}K$	
(b) 80% CO_2 and 20% N_2 and/or Ar -- $175^{\circ}K$	
Surface number density	
(a) All CO_2 -- 1.9×10^{17} cm^{-3}	Fjeldbo et al. (ref. 11)
(b) 80% CO_2 and 20% N_2 and/or Ar -- 2.1×10^{17} cm^{-3}	
Surface scale height -- 9.0 km	
Temperature and density profiles	
Mariner 6	
Surface temperature -- $250^{\circ}K$	
Surface number density -- 1.7×10^{17} cm^{-3}	Rasool et al. (ref. 12)
Surface scale height -- 12.5 km	
Temperature and density profiles	

TABLE I. - PARAMETERS USED AND THEIR SOURCES - Continued

PARAMETERS	SOURCES
<u>MARINER 7</u>	
Surface temperature -- $224^{o}K$	
Surface number density -- 1.6×10^{17} cm^{-3}	Rasool *et al.* (ref. 12)
Surface scale height -- 11.2 km	
Temperature and density profiles	
Oxygen mixing ratio -- 10^{-3}	Belton & Hunten (ref. 14) McElroy & Hunten (ref. 8)
Solar flux on the top of Earth's atmosphere in 1350-7100 Å region	
7100 - 3000 Å	Craig (ref. 4)
3000 - 2500 Å	Johnson (ref. 15)
2500 - 1500 Å	Detwiler *et. al*. (ref. 16)
1500 - 1350 Å	Watanabe (ref. 17)
Average dilution factor to account for diminution of solar flux in vicinity of Mars -- $\mu = 0.4307$	

TABLE I. - PARAMETERS USED AND THEIR SOURCES - Continued

PARAMETERS	SOURCES
Absorption cross sections:	
O_2: 2800 - 2000 Å	Shardanand (ref. 18)
2000 - 1750 Å	Gast (ref. 19)
1750 - 1350 Å	Watanabe (ref. 20)
CO_2: 2200 - 1750 Å	Fabian & Libby (ref. 7)
1750 - 1350 Å	Watanabe *et al*. (ref. 21)
O_3: 7100 - 3000 Å	Craig (ref. 4)
3000 - 2000 Å	Inn & Tanaka (ref. 22)
2000 - 1350 Å	Watanabe *et al*. (ref. 21)
Photodissociation yield factors for oxygen and ozone -- assumed to be unity	
Rate constants	
$k_2 = 5.5 \times 10^{-34} (T/300)^{-2.9}$ cm^6 molec^{-2} sec^{-1}	
$k_3 = 1.4 \times 10^{-12} \exp(-1500/T)$ cm^3 molec^{-1} sec^{-1}	Kaufman (ref. 23)
$k_5 = 3.0 \times 10^{-33} (T/300)^{-2.9}$ cm^6 molec^{-2} sec^{-1}	

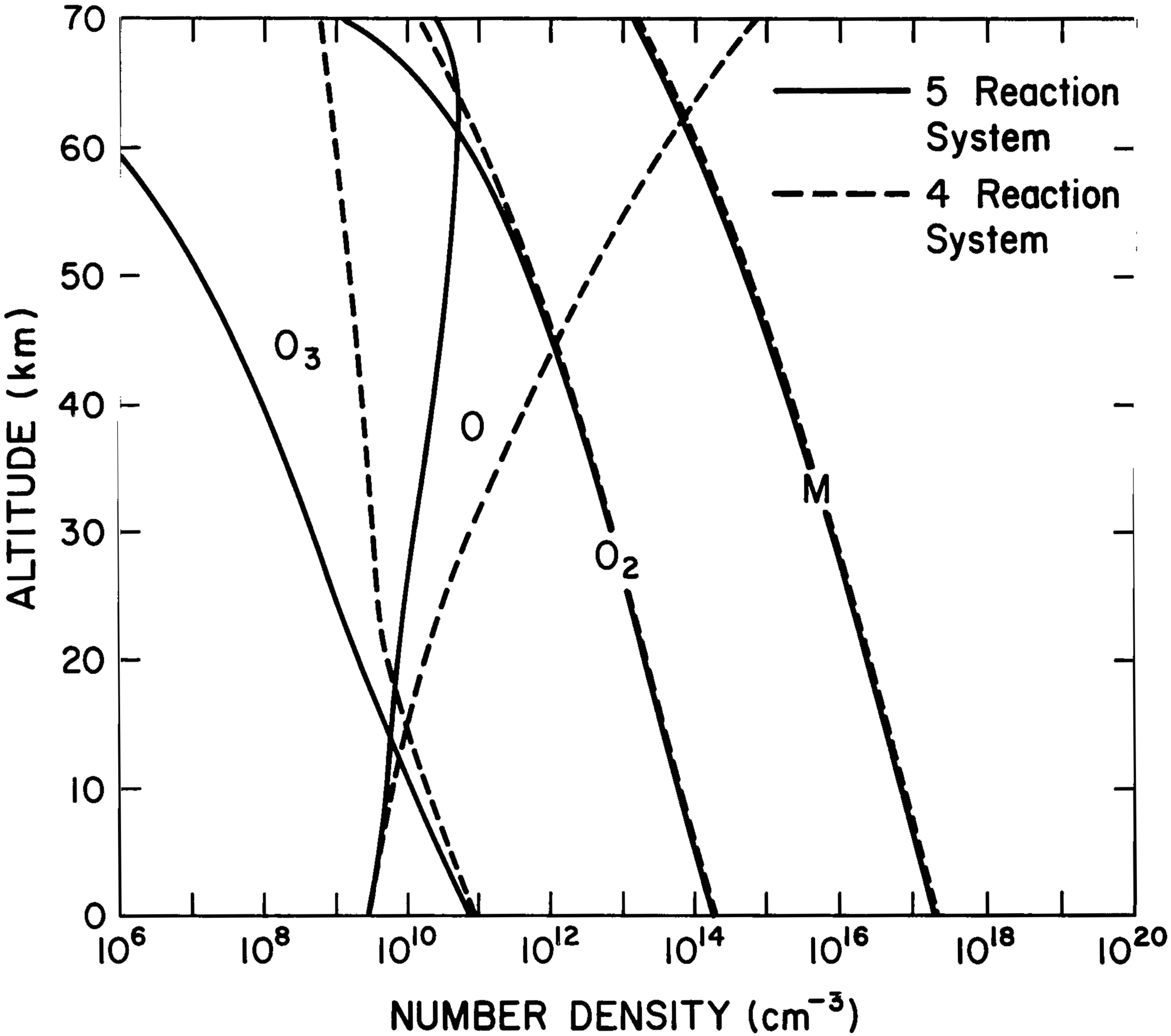

Figure 1 - Comparative profiles of oxygen compounds calculated from the 4-reaction and the 5-reaction systems for a model atmosphere based on the results of the Mariner 4 occultation experiment.

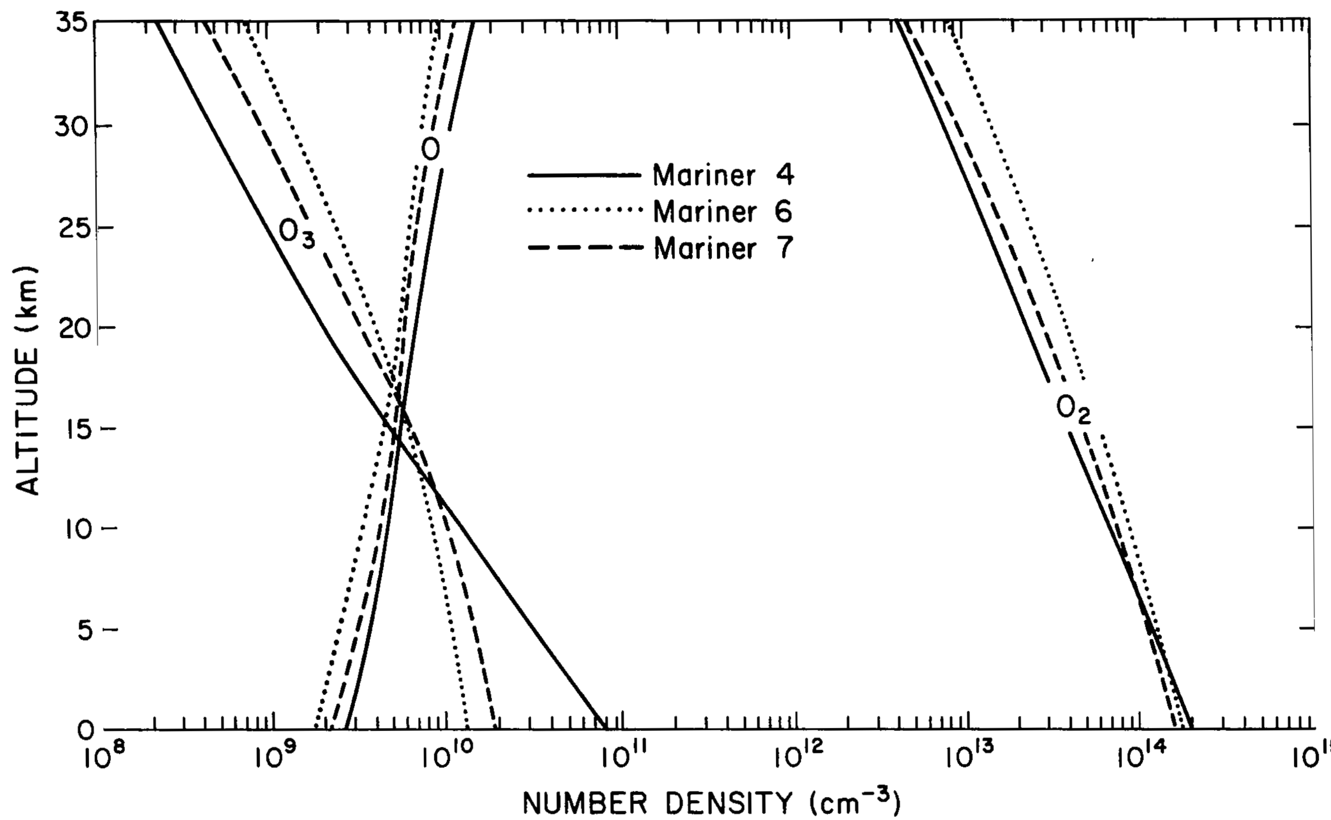

Figure 2 - Comparative profiles of oxygen compounds calculated from the 5-reaction system for model atmospheres based on the results of the Mariner 4, 6, and 7 occultation experiments.

REFERENCES

1. Hunt, B. G.: The Need for a Modified Photochemical Theory of Ozonosphere. J. Atmos. Sci., vol. 23, 1966, pp. 88-95.

2. Wulf, O. R.; and Deming, L. S.: The Theoretical Calculation of the Distribution of Photochemically-formed Ozone in the Atmosphere. Terr. Magn. Atmos. Elec., vol. 41, 1936, pp. 299-310.

3. Wulf, O. R.; and Deming, L. S.: The Distribution of Atmospheric Ozone in Equilibrium with Solar Radiation and the Rate of Maintenance of the Distribution. Terr. Magn. Atmos. Elec., vol 42, 1937, pp. 195-202.

4. Craig, R. A.: The Observations and Photochemistry of Atmospheric Ozone and their Meteorological Significance. Meteorol. Monographs, vol. 1, no. 2, 1950, pp. 1-50.

5. Paetzold, H. K.: On the Problems of the Martian Ozonosphere. Mem. Soc. Roy. Sci. Liege, vol. 7, 1963, pp. 452-459.

6. Marmo, F. F.; Shardanand; and Warneck, P.: Ozone Distribution in the Atmosphere of Mars. J. Geophys. Res., vol. 70, 1965, pp. 2270-2272.

7. Fabian, P.; and Libby, W. F.: Ozone in the Atmosphere of Venus, Zeitschrift fur Geophysik, vol. 35, 1969, pp. 1-7.

8. McElroy, M. B.; and Hunten, D. M.: Photochemistry of CO_2 in the Atmosphere of Mars. J. Geophys. Res., vol. 75, 1970, pp. 1188-1201.

9. Kaplan, L. D.; Munch, G.; and Spinrad, H.: An Analysis of the Spectrum of Mars. J. Astrophys., vol. 139, 1964, pp. 1-15.

10. Schilling, G. F.: Limiting Model Atmosphere of Mars. Rept. R-402-JPL, 1962, Rand Corporation, Santa Monica, California.

11. Fjeldbo, G.; Fjeldbo, W. C.; and Eshleman, V. R.: Models for the Atmosphere of Mars Based on the Mariner 4 Occultation Experiment. J. Geophys. Res., vol. 71, 1966, pp. 2307-2316.

12. Rasool, S. I.; Hogan, J. S.; and Stewart, R. W.: Temperature Distributions in the Lower Atmosphere of Mars from Mariner 6 and 7 Radio Occultation Data. J. Atmosph. Sci., vol. 27, 1970, pp. 841-843.

13. Barth, Charles A.; and Hord, Charles W.: Mariner Ultraviolet Spectrometer: Topography and Polar Cap. Science, vol. 173, 1971, pp. 197-201.

14. Belton, M. J. S.; and Hunten, D. M.: A Search for O_2 on Mars and Venus: A Possible Detection of Oxygen in the Atmosphere of Mars. J. Astrophys., vol. 153, 1968, pp. 963-974. (Erratum. J. Astrophys., vol. 156, 1969, p. 797).

15. Johnson, F. S.: The Solar Constant. J. Meteorol., vol. 11, 1954, pp. 431-439.

16. Detwiler, C. R.; Garrett, D. L.; Purcell, J. D., and Tousey, R.: The Intensity Distribution in the Ultraviolet Solar Spectrum. Ann. Geophys., vol. 17, 1961, p. 263.

17. Watanabe, K.: The Solar Spectrum and Cross-sections for Photoionization and Absorption in Atmospheric Processes, by P. J. Nawrocki and R. Papa, Pergamon Press, New York, 1962.

18. Shardanand: Absorption Cross-sections of O_2 and O_4 between 2000 and 2800 Å. Phys. Rev., vol. 186, 1969, pp. 5-9.

19. Gast, P. R.: Handbook of Geophysics, Revised ed., chapter 16, p. 25, The Macmillan Company, New York, 1961.

20. Watanabe, K.: Ultraviolet Absorption Processes in the Upper Atmosphere. Advances in Geophysics, vol. 5, 1958, edited by H. E. Landsberg and J. Van Mieghem, Acamdemic Press, New York.

21. Watanabe, K.; Zelikoff, M.; and Inn, E. C. Y.: Absorption Coefficients of Several Atmospheric Gases. AFCRL Tech. Rept. 53-23, Geophysical Research Paper 21, 1953, Geophysics Resarch Directorate, Cambridge, Massachusetts.

22. Inn, E. C. Y.; and Tanaka, Y.: Ozone Absorption Coefficients in the Visible and Ultraviolet Regions in Ozone Chemistry and Technology: Advances in Chemistry, Series 21, p. 263, American Society, Washington, D. C., 1959.

23. Kaufman, F.: Neutral Reactions. DASA Reaction Rate Handbook, Defense Atomic Support Agency, Washington, D. C., 1967.

NASA-Langley, 1972 —— 13

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546